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Magnetic properties of bismuth telluride (Bi_2Te_3) crystals

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Rhombohedral single crystals of Bi_2Te_3 (both p and n types) were prepared by horizontal zone melting apparatus set up here. The magnetic susceptibility along both the principal crystallographic directions were measured over the temperature range 90° to 650°K. The magnetic susceptibility due to carriers was separated out from the observed susceptibility From this the energy gaps in both the principal directions were calculated and compared with values obtained from electrical measurements.

INTRODUCTION

Various properties such as the electrical and thermal conductivities, Hall effect, Seebeck effect and magneto-resistance etc, of bismuth telluride (Bi_2Te_3), the thermoelectrically important semiconductor, have been studied by a number of workers (Shigetomi *et al* 1956, Satherwaite *et al* 1957, Goldsmid 1957, Mansfield *et al* 1958, Drabble *et al* 1958, Delves *et al* 1961, Caywood *et al* 1970).

But investigations on its magnetic properties are rather scanty. Matyas (1958) measured the magnetic susceptibility of polycrystalline Bi_2Te_3 over the temperature range of 100° to 500°K and found it to be diamagnetic, its susceptibility being temperature independent Mansfield (1959) measured the principal diamagnetic susceptibilities of Bi_2Te_3 single crystals over the temperature range of 100° to 600°K and found that the diamagnetic susceptibilities (the principal susceptibilities as well as the average value) are temperature dependent. But he could not separate the carrier susceptibility from the observed suseiptibility and therefore could not discuss his observations in relation to the existing theories of magnetic properties of charge carriers. Van Deynse *et al* (1969) measured the susceptibility of Bi_2Te_3 crystals from 1.3° to about 300°K. Obviously their measurements are confined to the extrinsic region only, and therefore not expected to throw any light on the intrinsic behaviour of the substance We have therefore undertaken to study the magnetic properties of both n and p type single crystals of Bi_2Te_3 over the temperature range 90° to 650°K. An account of these measurements are given in the present communication.

EXPERIMENTAL

Preparation of the crystals

The crystals were prepared in the laboratory by the horizontal zone melting process in an apparatus set up by us. The apparatus is a modified form of the one described by Cressel & Powel (1957). It consists of various components, *viz.* a speed adjustable (within the range 0.4 to 10 cms/hour) moving furnace, two water-cooled steel muffles to adjust the zone width, accompanying vacuum system, inert gas flushing system etc. The different parts of the unit are diagramatically represented in figure 1.

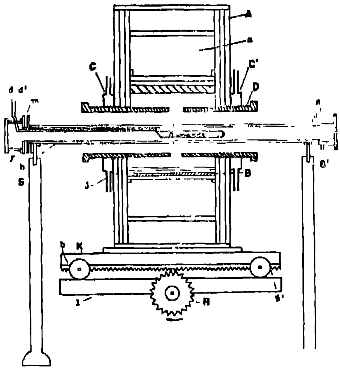

Figure 1. Schematic diagram of the horizontal zone-melt crystal growing furnace.

A—Furnace housing
B—Nichrome element
C, C'—Water cooled jacket
D—Adjustable muffle
d d'—Thermocouple elements
e, e'—Glass windows
f—Gas outlet
g—Brass end closure
h—Silica tube
a—Quartz crucible with molten zone
b, b'—Ball race
m—Gas inlet
j—Porcelain tube
K—Saddle trolley
l—Precision bed
n—Thermal insulation
S, S'—Adjustable holder
R—Electric motor driven wheel (with gear-down attachment)

For the preparation of Bi_2Te_3 we used 99.98% pure Bi and 99.97% pure Te. We purified further the Bi and Te components separately by the zone-melting process A quantity of Bi was put in a quartz ampoule of about 5 cms length and 1 cm bore which was sealed after evacuation to $\sim 10^{-5}$ mm of Hg The furnace with zone width 3 mm was made to pass over the charge of Bi ten times in one direction only at the rate of 0.5 cm/hr. The temperatre of the zone was kept at some value higher than the melting point (271.3°C) of Bi. The parts of the ingot which had solidified first had the highest degree of purity. But Te being similarly treated, evaporated and condensed on the inner surface of the ampoule. We therefore kept Te in the ampoule in an argon gas atmosphere (the pressure was slightly less than the atmospheric pressure) and purified it in the usual way. Bi and Te thus refined were put in requisite proprotions in a similar quartz ampoule which was sealed after being filled with argon gas at a pressure slightly lower than the atmospheric pressure. The ampoule was then placed inside the silica tube over which the furnace with the same zone width can traverse lengthwise. The furnace was now allowed to traverse the ingot ten times in one direction only at the rate of 0.5 cm/hr. The temperature of the melt was kept at about 650°C. After these operations were over, the ampoule was broken and the single crystal obtained from the ingot. For p-type specimens a slight excess of Bi ($\sim$ 0.2%) and for n-type that of iodine ($\sim$ 0.2%) were used as dopants The specimens were then chemically analysed and tested by X-rays.

The basic unit cell is rhombohedral but for electrical and magnetic work the corresponding hexagonal unit cell is frequently used. We have found from our X-ray data, $a = 4.384$Å and $c = 30.487$Å, the three fold axis or the c-axis of the hexagonal system is normal to the direction of crystal growth.

Magnetic Measurement

The crystals are of uniaxial type with easy cleavage, the c-axis being perpendicular to the cleavage plane. Therefore for the anisotropy as well as absolute susceptibility measurements, observations with the cleavage plane vertical would be sufficient.

(*i*) *Anisotropy*

A single crystal of Bi_2Te_3 with a perfect cleavage plane was chosen and its mass measured with a Mettler microbalance (least count 5×10^{-6} gm). It was attached with its cleavage plane vertical at one end of a calibrated quartz fibre, the other end being fixed to a graduated torsion head. The entire system was so placed that the crystal remained suspended inside a homogeneous horizontal magnetic field. The anisotropy of the crystal was then measured by the usual "null method" developed in this laboratory (Dutta, 1954).

(*ii*) *Susceptibility*

For the measurement of susceptibility, the crystal was suspended with its cleavage plane vertical by a quartz fibre. from the free end of the arm of a jewel pivoted microbalance (Das 1963) and placed in a horizontal magnetic field with a vertical gradient, such that the magnetic force remained constant over an appreciable region (Sucksmith 1939, Dutta-Ray 1955). The magnetic force on the sample when the field was switched on was balanced by an electrodynamic balancing device (Das 1963) attached at the other end of the balance beam.

All measurements were made in dark and vacuum. For low temperature measurements the crystal remained inside the experimental chamber of a gas flow liquid oxygen cryostat (Bose 1947), the temperature of the chamber being recorded by a calibrated copper-constantan thermocouple For measurements at high temperatures the crystal was kept within the experimental chamber of a cylindrical furnace non-inductively wound on the outside with nichrome wire The temperature in this case was measured by calibrated chromel-alumel thermocouple.

Results and discussions

The crystal suspended with the cleavage plane vertical (c-axis horizontal) was found to set with this plane along the magnetic field and its susceptibility was diamagnetic. Therefore $\chi_\perp$, the susceptibility per unit mass in the cleavage plane was algebraically greater than $\chi_{\parallel}$, that along the c-axis. Therefore the measured anisotropy was $\chi_\perp - \chi_{\parallel}$ and the susceptibility measured $\chi_\perp$.

The values of $\chi_\perp - \chi_{\parallel}$, $\chi_\perp$ and $\chi_{\parallel}$ at different temperatures are given in figure 2. The values of $\bar{\chi}$ the average susceptibility, and $\chi_\perp/\chi_{\parallel}$ the ratio of susceptibilities, at 300°K of various authors including the present are given in table 1.

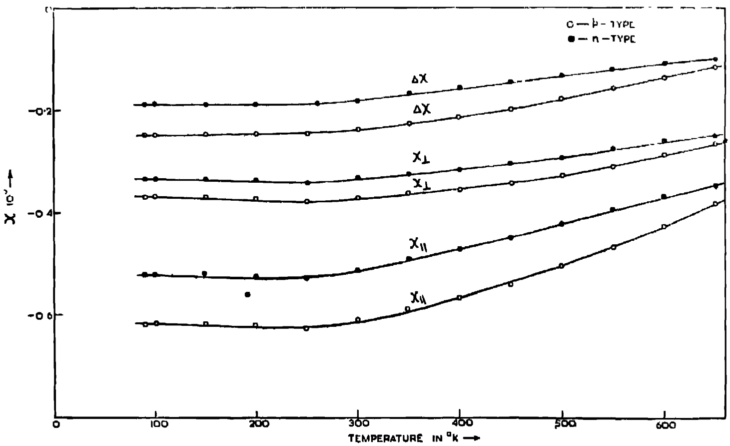

Figure 2. The variation of mass susceptibility of Bi_2Te_3 with temperature.

It is observed from our results plotted in the figure 2 that both $\chi_\perp - \chi_{\parallel}$ and $\chi_\perp$ numerically increase with the lowering of temperature and ultimately attain a temperature independent value.

Now with the increase of temperature the thermally excited free carriers increase exponentially; but from the nature of the curve (figure 2), it is found that the total diamagnetic susceptibility gradually decreases with the increase of temperature, suggesting thereby that contributions due to the excited free carriers is paramagnetic, which can be separated as follows.

Table 1

Author	Mean mass susceptibility at 300° $\bar{\chi} \times 10^6$	Anisotropy ratio ($\chi_{\parallel}/\chi_{\perp}$) at 300°K	Susceptibility of carriers
Matyas (1958)	-0.402		
Mansfield (1958)	-0.462		Paramagnetic
Van Deynse *et al* (1969)	-0.485	1.63	
Present Authors	-0.451 (*p*-type) -0.392 (*n*-type)	1.64 (*p*-type) 1.54 (*n*-type)	Paramagnetic

The observed susceptibility χ of a semiconducting system may be assumed to be composed of χ_L the lattice susceptibility, χ_c the susceptibility due to free carriers, and χ_I the susceptibility due to impurity centres (impurity atoms or lattice defects).

Algebraically,

$$\chi = \chi_L + \chi_c + \chi_I. \tag{1}$$

χ_L was thought to be a diamagnetic term which is essentially temperature independent. But Krumhansl & Brooks (1956) have shown that this should also include a paramagnetic term, somewhat analogous to the high frequency Van Vleck paramagnetism, but having a small temperature dependence of the same order as that of the band gap, which, however, for ordinary temperatures may be neglected. χ_c contains two temperature dependent terms : a paramagnetic term due to the spin of free carriers and a diamagnetic term due to their orbital motions in a magnetic field χ_I also contains two terms : a temperature independent diamagnetic contribution of the core and valance electrons of the impurity atoms and a paramagnetic temperature dependent term due to the net magnetic moment. Therefore in our case χ may be written as

$$-\chi = \pm\chi_0 \pm \chi_c(T) + \chi_I(T) \tag{2}$$

where X_0 is the temperature independent susceptibility arising out of all the different contributions and χ the observed susceptibility.

Now assuming a simple Curie law for the temperature variation of χ_I and plotting χT against T, we could find the contribution of χ_I at different temperatures (which in our case was actually found to be very small, a fact also evident from the temperature independence of χ at low temperatures). It may be pointed out in this connection that the effect of χ_I which arises out of the ionized and non-ionized impurity centres, is generally considered negligible and from electrical measurements it was found that the impurities were all ionized even below 100°K. Mansfield (1958) neglected the effect due to impurity. From the low temperature portion of the curve obtained by plotting χ_{obs} *vs* T (figure 2), after eliminating χ_I, χ_0 could be found and it appeared to be diamagnetic. Subtracting χ_0 and χ_I from χ_{obs} we obtained χ_c, the contribution due to free carriers which obviously is paramagnetic, and increases with the temperature.

Now it is well known (Busch & Mooser 1953) that the charge-carrier susceptibility of a semiconductor in the intrinsic range is given by

$$\chi_c = AT^{\frac{1}{2}}e^{-E_g/2kT}\,; \tag{3}$$

where A is a constant containing the appropriate effective masses of carriers, E_g the activation energy and the rest of the symbols have their usual significance. Plotting $\log \chi_c T^{-\frac{1}{2}}$ against $1/T$, the resulting curve (figure 3) is found to have a straight portion within the temperature range 400° to 650°K, which we know from our electrical conductivity measurements to be well within the intrinsic region.

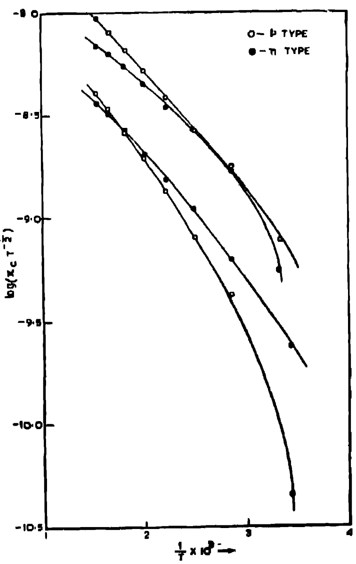

Figure 3. $\log(\chi_c T^{-\frac{1}{2}})$ as a function of temperature

Uppercurves refer to the cases when the magnetic field is parallel to the c-axis.

Lowercurves refer to the cases when the magnetic field is perpendicular to the c-axis

From the slope of the straight line portion E_g's were calculated and from the intercept the values of A were determined. The values of these parameters for different directions and for both p-and n-type specimens are given in table 2.

Table 2

	Crystallographic direction	By magnetic measurements		By electrical measurements
		$A \times 10^8$	E_g in *ev*	E_g in *ev*
p-type Bi_2Te_3	Along c-axis	5 89	0.21	0.20
	Perpendicular to c-axis	2 24	0.21	0.20
n-type Bi_2Te_3	Along c-axix	4.17	0.19	0.20
	Perpendicular to c-axis	1 91	0.19	0.20

The corresponding values of E_g obtained from electrical conductivity measurements are indicated in table 2 It is observed that the values of E_g obtained from two measurements may be considered to compare, in general, well with each other

It is found from figure 3 that the curve deviates from linearity at lower temperatures. This may be due to the predominance of the effect of a constant number of extrinsic carriers in the valence or conduction band (due to very small activation energy, all the impurity centres are ionized at very low temperature and this remains constant till the intrinsic carriers are set free) Within the purely extrinsic region of our measurements *i.e.*, below 250°K, where the carrier numbers as pointed out above are constant, the carrier susceptibility is an admixture of degenerate and non-degenerate regions.

A complete discussion of these effects as also the evaluation of the different fundamental parameters involved in A, requires the development of a theory for single crystals, which has recently been worked out here and calculations are in progress. This will be published in a subsequent paper.

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